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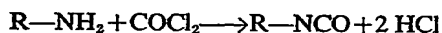
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COMPLETE SPECIFICATION.

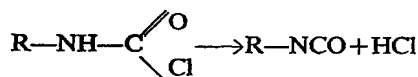
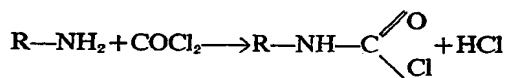
A Process for the Continuous Preparation of Aromatic Mono- and Diisocyanates.

We, CHEMOKOMPLEX VEGYIPARI GEP ES BERENDEZES EXPORT-IMPORT VALLALAT, a body corporate organised under the laws of Hungary of 64, Népköztársaság utja, Budapest VI, Hungary, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

Among the known processes for preparing isocyanates the one best suited for industrial realization is the process in which suitable amines and phosgene are used as starting materials, and in which the following reaction takes place:



This reaction consists of two steps and can be sub-divided into the following two reaction schemes:



In the first step carbamyl chloride is formed at low temperature; in the second step, after hydrogen chloride has been split off, the carbamyl chloride is decomposed into isocyanate at elevated temperatures (at least 100°C). The evolved hydrochloric acid forms a salt with the amine, the hydrochloric salt of the amine also reacts with the phosgene and is converted into isocyanate at a suitable temperature.

Various methods have become known for carrying out the above reaction in practice.

[Price]

In one group of precesses suited for industrial use the reaction is carried out in two steps. The first step is the so-called cold phosgene treatment, where a suspension or solution of the starting amine, for example a solution or suspension of the amine in carbonic acid, is reacted in the cold with phosgene or a solution of phosgene in an inert solvent. In the second step, the so-called warm phosgene treatment, phosgene is introduced into the reaction mixture at elevated temperatures until the conversion takes place at the maximum rate to be achieved.

According to the German Specifications Nos. 949,227, 949,228 and 952,086 the reaction of amines with phosgene is performed in two steps. In order to reduce the amount of phosgene required, i.e. to increase the yield, in the first step a mixture is prepared from the reactants and the mixture is treated for example at ambient temperature with phosgene. The reaction then proceeds in the second step at the temperature of warm phosgene treatment in either continuous or batch process, e.g. in tubular reaction vessels. By these known processes the isocyanate end product can be obtained with a yield of 70 to 80% calculated on the starting amine. The technological equipment and apparatus required for putting into practice this process involves high costs, whereas the warm phosgene treatment requires a comparatively high excess of phosgene. Owing to the length of the reaction period the end product becomes increasingly tarry.

In U.S. Patent Specification No. 2,683,160 a process is described for preparing isocyanates in one step omitting the step of cold treatment with phosgene. According to this process, 90 to 92% phosgene is used, calculated on the starting amine in a batch

process using one reaction vessel, but the stoichiometric excess of phosgene over the amine is at least 80 to 100%. The reduction of excess phosgene involves a reduction of the yield. Another disadvantage of this process, in addition to the extremely high excess of phosgene, is that with continuous or semi-continuous operation amine in an amount corresponding to the equilibrium value escapes from the reaction vessel together with the isocyanate, whereby the yield calculated on the end product is considerably reduced.

It is clear, therefore, that with the known processes a 80 to 100% stoichiometric excess of phosgene will only produce a 90 to 92% conversion at the most. The one-step reaction can be carried out economically only as a batch process.

The object to be achieved is therefore to reduce the excess of phosgene required for preparing the isocyanates on the one hand, to further increase the yield and to cut down to a minimum the amount of by-products due to side reactions.

It has been found that it is possible to prepare aromatic mono-isocyanates and diisocyanates in a continuous process by reacting monoamines or diamines with phosgene in an organic solvent medium in the temperature range of the so-called warm phosgene treatment, i.e. in the range of 120 to 200°C with an improved yield and using a smaller amount of phosgene than conventionally, if the phosgene treatment of the starting amine is performed successively in two coupled reaction vessels with an excess of phosgene of between 5 and 20% calculated on the stoichiometric amount.

Preferably one proceeds in the following manner: The first step of the reaction is carried out instantaneously with continuous introduction of phosgene and amine in the first reaction vessel containing phosgene dissolved in a preheated organic solvent, up to a conversion of about 75 to 88%, using approximately the stoichiometric amount of phosgene. In the second step the amount of phosgene used for treating the partly converted reaction mixture is such as to produce a 5 to 20% stoichiometric excess. Hence, the reaction can be carried out almost to complete conversion in the second reaction step.

Preferably the reaction vessels are coupled in a cascade system.

The process according to the invention can be carried out continuously in two heatable reaction vessels consisting of acid-resistant steel, conveniently provided with a turbo agitator. The reaction vessels are fitted with inlets for the introduction of phosgene and dissolved amine, and with outlets for withdrawal of the reaction mixture and the end product. A reflux cooler

is also attached for withdrawing the excess phosgene and the hydrogen chloride gas evolved during reaction.

At the start of the reaction the amine solution, preheated to 100°C, is introduced into the first reaction vessel simultaneously with the phosgene, in which a phosgene solution heated up to its boiling point and dissolved in an organic solvent had been previously placed. When choosing the solvent essential considerations are that it has to remain inert in the reaction, and that hydrogen chloride should be sparingly soluble in it whereas phosgene should be readily soluble in it. The boiling point of the solvent must be below that of the amine, and is preferably in the range from 120 to 160°C. Accordingly, chlorinated aromatic hydrocarbons, for example o-dichlorobenzene are suitable. The amine is preferably used in a 15% solution.

If the phosgene is added in a stoichiometric amount calculated on the amine, then the reaction takes place in the first reaction practically instantaneously, with an about 75 to 88% conversion and free of by-products.

The reaction mixture, converted up to about 85%, is transferred from the first reaction vessel through an overrun, preferably by gravity force, into a second reaction vessel which is substantially identical in structure and kept at the same temperature as the first vessel. Simultaneously phosgene is admitted into the second reaction vessel in such an amount that the total amount of phosgene introduced into the two reaction vessels amounts to 1.05 to 1.2 times the amount stoichiometrically required for completing the reaction.

The preferred temperature for the reaction varies within the range between 120 and 200°C depending on the amine component employed. The yield to be achieved is considerably reduced, if one works above or below said temperature range.

In the second reaction vessel the isocyanate is formed with a 93 to 96% conversion rate, calculated on the total amine amount introduced. The reaction mixture leaving the second reaction vessel is transferred to a collecting vessel where the hydrogen chloride and the small amount of residual phosgene is flushed out by an inert gas, for example nitrogen.

The isocyanate obtained as end product of the process according to the invention is of very high purity. After removing by vacuum distillation the minimum of impurity present and the solvent, an isocyanate of practically 100% purity is obtained. The solvent containing a little isocyanate obtained as a forerun of distillation is recycled to the first step without any separate cleaning operation. The insignificant amount of

excess phosgene departing from the two reaction vessels may also be recycled after being freed from hydrochloric acid.

In view of the generally prevailing level of the art it is surprising to find that isocyanates can be obtained in a solvent, at the temperature of what is commonly termed "warm phosgene treatment", by reacting amines with phosgene in two consecutive steps but under identical conditions of reaction, practically without side reactions, with a yield of 93 to 96% and with a smaller excess of phosgene than in the conventional processes. With the aid of the invention this may be achieved by means of relatively simple apparatus, i.e. by introducing the phosgene component in two steps into two reaction vessels containing a phosgene solution and connected in a cascade system.

The process according to the invention is extremely well suited for producing aromatic isocyanates on an industrial scale, since it lends itself to be carried out in a simple apparatus with a good yield, so that one can achieve an end product of high purity without having to resort to a complicated technology.

The invention is more particularly described below by the following illustrative examples:

EXAMPLE 1

Into a heatable acid-resistant steel reaction vessel of 2.8 litres volume fitted with a reflux condenser and turbo agitator, containing *o*-dichlorobenzene saturated with phosgene having a temperature of 160°C, the introduction of 2,6-tolylene-diamine dissolved in 15% *o*-dichlorobenzene and pre-heated to 100°C is started simultaneously with phosgene. The amine solution is introduced at a rate of 6 g. amine per minute, and phosgene at a rate of 9.6 g. per minute. The reaction mass is transferred from the first to the second reaction vessel through an overflow pipe. Phosgene is admitted to the second reaction vessel at the rate of 1.9 g. per minute. The reaction temperature is 160°C in both reaction vessels. The reaction mixture is freed from phosgene and hydrogen chloride by flushing with dry nitrogen, also at 160°C. The reaction mixture is subjected to vacuum distillation. The solvent obtained as forerun is recycled. 2,6-tolylene-diisocyanate is obtained with a yield of 94% calculated on the amine, with a 99.9% purity.

EXAMPLE 2

One proceeds in a manner similar to Example 1, with the difference that 2,4-tolylene-diamine is used as amine component. A 96% yield of 2,4-tolylene-diiso-

cyanate, calculated on the amine, is obtained. This product analyzes 100% purity.

EXAMPLE 3

The process is similar to that in Examples 1 and 2, with the difference, however, of using a mixture of 2,4-tolylene-diamine and 2,6-tolylene-diamine in a 80 to 20 ratio as amine component. The isocyanate isomers are obtained in a similar ratio with 100% purity. The yield, calculated on the amine, amounts to 95%.

EXAMPLE 4

Diphenyl-methane-*p,p'*-diamine is reacted with phosgene in accordance with Example 1. Diphenylmethane-*p,p'*-diisocyanate is obtained in a 99.8% purity. Amine is introduced at a rate of 6 g. amine per minute, phosgene at a rate of 6 g. per minute in the first reaction vessel and at a rate of 1.1 g. per minute in the second.

WHAT WE CLAIM IS:—

1. A process for the continuous preparation of an aromatic mono-isocyanate or diisocyanate by reacting a monoamine or diamine, respectively, with phosgene in an organic solvent medium at the temperature of the so-called warm phosgene treatment, i.e. in the range of 120 to 200°C, in which the starting amine is reacted with the phosgene successively in two coupled reaction vessels, using an excess of phosgene of between 5 and 20% calculated on the stoichiometrically required amount.

2. A process as claimed in Claim 1, in which a pre-heated solution of phosgene in an organic solvent is placed in the first reaction vessel, then the conversion is carried out up to 75 to 88% by the continuous introduction of phosgene and amine, finally the phosgene treatment of the partly converted reaction mixture is completed in the second reaction vessel.

3. A process as claimed in Claim 1 or Claim 2 in which the reaction is carried out in two reaction vessels coupled in a cascade system.

4. A process for the preparation of an aromatic isocyanate substantially as hereinbefore described with reference to any one of the Examples.

5. An aromatic mono-isocyanate or diisocyanate when prepared by a process as claimed in any of Claims 1 to 4.

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